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REGULAR ARTICLE

Electronic structures of 4d transition metal monoxides by density functional theory

P. Song · W. Guan · C. Yao · Z. M. Su · Z. J. Wu · J. D. Feng · L. K. Yan

Abstract Bond distances, dissociation energies, ionization potentials and electron affinities of 4d transition metal monoxides from YO to CdO and their positive and negative ions were studied by use of density functional methods B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, SVWN, MPW1PW91 and PBE1PBE. It was found that calculated properties are highly dependent on the functionals employed, especially for dissociation energy. For most neutral species, pure density functionals BLYP, BPW91 and BP86 have good performance in predicting dissociation energy than hybrid density functionals B3LYP, B3PW91 and B3P86. In addition, BLYP gives the largest bond distance compared with other density functional methods, while SVWN gives shortest bond distance, largest dissociation energy and electron affinity. For the ground state, the spin multiplicity of the charged species can be obtained by ±1 of their corresponding neutral species.

Keywords Density functional theory · Dissociation energy · Ionization potential · Electron affinity

1 Introduction

Diatomic molecules containing a single species bound to transition metals are of considerable importance as models to further our understanding of the fundamental nature of chemical bonds involving transition metal elements. In particular, understanding the nature of chemical bond between a transition metal and a main group element is of great interest in many areas of science, e.g., surface chemistry, catalysis, astrophysics and organometallic chemistry. Recently, the electronic structures of diatomic molecules MX (M = transition metal, X = main group element), which are composed of 3d transition metal and main-group element H, Li, B, C, N, O and F, has been reviewed [1]. For 3d transition metal hydrides MH (M = Sc–Cu), diverse theoretical studies were available [2–6]. For 3d transition metal oxides MO and transition metal carbides MC (M = Sc–Zn) of neutral, cation and anion species, systematic study was conducted by diverse density functional methods (DFT) [7]. In addition, the ground and low-lying excited states of neutral 3d transition metal monoxides and monosulfides were also studied by non-local density functional methods [8]. The 3d transition metal phosphides MP (M = Sc–Cu) in neutral form was studied by DFT [9]. For 4d transition metals, systematic theoretical study was given by use of modified coupled pair functional (MCPF) method on monoxides MO and carbenes MCH_2 (M = Y–Pd) [10]. Theoretical studies for individual species also include the spectroscopic constants of monoxides and monosulfides of Y, Zr and Nb by MCPF method [11]; MoO, PdO and AgO by configuration interaction (CI) plus Davidson's correction (denoted as CI + Q) [12] and MCPF calculation on bond distance of MoO and AgO [13]. Meanwhile, AgO was also investigated

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P. Song · W. Guan · C. Yao · Z. M. Su (✉) · J. D. Feng · L. K.Yan
Faculty of Chemistry, Institute of Functional Material Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China
e-mail: zmsu@nenu.edu.cn

Z. J. Wu (✉)
Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
e-mail: zjwu@ciac.jl.cn

by diverse density functional methods [14]. The recent experimental study by photoelectron spectroscopy was available for YO and its anion YO^-, PdO and its anion PdO^- [15], in which the electron affinity of YO and PdO was obtained. We are unaware of any studies on the charged species except for YO^- and PdO^-.

It is known that multireference correlation must be considered in many transition metals compounds and some molecules with strong configuration correlation effect. Multireference situations are found not only in metals but also in nonmetallic bond-breaking processes and in many transition states and open-shell molecules. However, it is known that these multireference methods are very time-consuming, and it would be a formidable task, if not impossible, for the current research because there are thousands of structures that need to be optimized.

DFT is widely used to determine structures of molecules currently. Compared to high-level ab initio molecular orbital theories, DFT has the advantage of applicability anywhere in the periodic table and inherent computational efficiency. This makes it particularly effective for those molecules involving heavy metal elements. Many density functional methods have been developed during the past decades [16]. In addition, by proposing the approximate spin projection in the study of Cr2, Becke et al. found ways to correct the multireference character in DFT study [17], which makes DFT more promising. In addition, Truhlar et al. compared the performance of diverse hybrid DFT methods with pure DFT methods, and introduced a parameter named B1 diagnostic to provide a measure of multireference character in a bond [18]. This opens the way for future study in recognizing the multireference character of a system.

In this study, we chose DFT because comparing with the traditional correlation techniques, it has moderate accuracy, fast and much-reduced basis set requirements. At the same time, it is necessary and meaningful for these methods to see how they perform on different systems, especially for those containing transition metals because different density functional methods may produce quite different properties (e.g., different ground state) for a given system [7,14,16]. In this study, the ground state of the 4d transition metal monoxides was determined by the use of diverse density functional methods. The results are compared between different density functional methods and compared with the available experiments and previous theoretical studies. We hope this work could stimulate more researches on transition metals with different ligands and provide reference in choosing the reliable density functional method in future study.

2 Computational methods

All geometry optimizations were performed by the use of the Gaussian03 suite of programs [19]. Equilibrium geometries and corresponding electronic properties were determined for the studied species by the use of nine different exchange–correlation functionals, denoted as B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, SVWN, MPW1PW91 and PBE1PBE [20–30]. For these density functional methods, the correlation functional is from either Lee, Yang and Parr (LYP) [20], Perdew–Wang 1991 (PW91) [21], or Perdew 86 [22], while the exchange functional is from either Becke's three-parameter HF/DFT hybrid exchange fuinctional (B3) [23], pure DFT exchange functional of 1988 (B) [24], Perdew–Wang 1991 (PW91) [21] or Barone's modified PW91 (MPW1) [25]. PBE1PBE is the GGA exchange–correlation functionals of Perdew et al. [26]. SVWN is the older local spin density approximation (LSDA), which utilizes the 1980 correlation functional of Vosko et al. [27] along with Slater exchange functional [28–30]. The basis set used in this study is Stuttgart/Dresden effective core potentials (ECPs), i.e., SDD [31] in Gaussian package, for 4d elements. All-electron basis set 6-311+G(d) for O. The valence electrons considered are $4s^2 4p^6 4d^n 5s^2$ for $n = 1$–10 from Y to Cd (i.e., 28-core-electrons for 4d elements). To avoid trapping at local minima of the potential energy surface, a number of different initial geometries (bond distances) were adopted for each species. The calculated dissociation energies were corrected by the zero-point vibrational energies.

3 Results and discussion

The calculated results were collected in Tables 1–4. Due to the unfilled d orbital of the transition metals, each species were first calculated by use of B3LYP at various spin multiplicities in order to find the lowest spin state (Table 1). From Table 1, it is been seen that the calculated square of total spin ($S^{**}2$) is very close to its eigenvalues $s(s+1)$, indicating that the spin contamination is minor. In Table 2, besides ionization potential (IP) and electron affinity (EA), it also listed the bond distance, vibrational frequency and dissociation energy for the neutral species from the lowest spin multiplicity for various density functional methods, B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, SVWN, MPW1PW91 and PBE1PBE. Tables 3 and 4 listed the bond distance and vibrational frequency for cations and anions, respectively.

Table 1 Calculated bond distances d (Å), vibrational frequency ω (cm^{-1}), relative stability ΔE (eV) and spin contamination of neutral diatomic MO and charged species MO^{+}, MO^{-} (M = 4d Transition Metal Element) at possible spin multiplicities S at B3LYP Level

	YO				ZrO				NbO				MoO					TcO			
Neutral	2	4	6	8	1	3	5	7	2	4	6	8	1	3	5	7	9	2	4	6	8
d	1.830	2.117	2.894	3.708	1.744	1.761	2.022	4.285	1.698	1.710	2.011	2.755	1.661	1.665	1.723	2.035	3.908	1.641	1.689	1.752	2.137
ω	857.7	528.7	109.1	122.0	976.1	929.6	594.7	16.7	1019.9	982.7	597.0	123.1	1043.2	1023.4	920.5	560.8	28.1	1009.6	948.2	877.0	489.8
ΔE	0.00	3.08	8.29	17.38	0.15	0.00	3.52	7.79	0.75	0.00	3.50	7.07	1.25	0.34	0.00	2.22	4.95	1.26	0.54	0.00	2.51
S**2	0.75	3.75	8.75	15.8	0.00	2.01	6.00	12.0	0.76	3.77	8.75	15.8	0.00	2.07	6.04	12.0	20.0	0.78	3.77	8.76	15.8
Cation	1	3	5	7	2	4	6	8	1	3	5	7	2	4	6	8	10	1	3	5	7
d	1.783	2.025	2.699	4.299	1.715	1.956	2.530	3.917	1.669	1.676	1.917	2.561	1.626	1.652	1.940	2.579	3.722	1.585	1.653	1.712	1.985
ω	923.5	643.5	181.0	96.4	1018.3	687.2	240.7	106.1	1060.7	1044.1	688.5	207.1	1111.7	1018.8	654.1	193.6	99.07	1174.7	1041.5	799.0	600.3
ΔE	0.00	2.63	6.36	14.86	0.00	2.68	6.46	13.83	0.12	0.00	2.87	5.63	0.40	0.00	2.80	4.19	11.08	0.29	0.10	0.00	1.19
S**2	0.00	2.00	6.00	12.0	0.75	3.75	8.75	15.8	0.00	2.01	6.00	12.0	0.76	3.80	8.76	15.8	24.8	0.00	2.02	6.14	12.0
Anion	1	3	5	7	2	4	6	8	1	3	5	7	2	4	6	8	10	1	3	5	7
d	1.870	1.872	2.165	3.163	1.792	1.811	2.116	3.092	1.729	1.735	1.759	2.137	1.681	1.740	1.782	2.232		1.637	1.703	1.772	1.843
ω	797.0	761.8	472.2	69.9	876.6	825.2	459.8	69.5	952.3	933.5	856.3	449.8	999.4	885.7	804.2	377.8		1049.2	929.5	839.7	730.1
ΔE	0.00	1.51	4.27	9.35	0.00	1.21	4.45	9.25	0.71	0.00	0.77	3.99	0.40	0.00	0.19	2.76		1.24	0.61	0.00	0.74
S**2	0.00	2.00	6.00	12.0	0.77	3.76	8.75	15.8	0.00	2.10	6.02	12.0	0.79	3.84	8.77	15.8		0.00	2.05	6.10	12.0
	RuO				RhO				PdO				AgO					CdO			
Neutral	1	3	5	7	2	4	6	8	1	3	5	7	2	4	6	8		1	3	5	7
d	1.644	1.705	1.735	1.854	1.760	1.739	1.850	2.023	1.813	1.870	1.845	2.130	2.041	2.369	2.269	2.499		1.937	2.159	2.768	2.672
ω	918.3	924.5	857.7	708.9	799.1	799.2	677.1	354.0	712.1	567.9	641.5	236.2	456.7	89.0	186.6	201.4		557.1	374.9	128.7	177.4
ΔE	1.74	0.88	0.00	1.89	0.93	0.00	1.75	8.20	1.12	0.00	1.68	8.42	0.00	1.82	8.87	18.13		0.45	0.00	4.78	14.63
S**2	0.00	2.01	6.01	12.0	0.76	3.76	8.77	15.8	0.00	2.01	6.01	12.0	0.78	3.76	8.76	15.8		0.00	2.01	6.01	12.0
Cation	2	4	6	8	1	3	5	7	2	4	6	8	1	3	5	7		2	4	6	8
d	1.615	1.695	1.773	2.195	1.676	1.679	1.797	2.140	1.799	1.819	2.309		2.039	2.209	2.387			2.047	2.640		
ω	1019.6	945.1	776.9	295.7	950.6	936.5	705.8	226.9	637.0	642.3	178.3		388.4	195.5	175.8			476.6	178.4		
ΔE	1.06	0.00	0.28	3.74	1.18	0.00	0.01	3.99	0.86	0.00	4.01		1.99	0.00	3.61			0.00	0.55		
S**2	0.75	3.76	8.76	15.8	0.00	2.01	6.01	12.0	0.80	3.76	8.76		0.00	2.01	6.01			0.85	3.76		
Anion	2	4	6	8	1	3	5	7	2	4	6	8	1	3	5	7		2	4	6	8
d	1.678	1.750	1.826	1.868	1.743	1.747	1.813	1.858	1.852	1.879	1.850	2.073	1.952	2.154	2.258	2.183		2.071	2.203	2.944	2.914
ω	930.6	836.8	735.4	688.0	801.6	782.6	738.5	668.2	644.0	612.1	639.7	287.0	501.1	346.1	173.5	216.4		398.5	350.6	78.3	152.1
ΔE	0.93	0.00	0.56	3.59	1.10	0.00	0.45	3.68	0.00	0.09	3.59	9.62	0.07	0.00	3.96	10.38		0.00	2.38	6.83	16.23
S**2	0.77	3.83	8.76	15.8	0.00	2.06	6.01	12.0	0.75	3.78	8.76	15.8	0.00	2.01	6.01	12.0		0.77	3.76	8.76	15.8

Table 2 Calculated bond distances d (Å), vibrational frequency ω (cm^{-1}), dissiciation energy D_e (eV), ionization potential IP (eV) and electron affinity EA (eV) of neutral MO at ground state

	S	YO	ZrO^{a}	NbO	MoO	TcO	RuO	RhO	PdO	AgO	CdO
		$^2\Sigma^+$	$^3\Delta$	$^4\Sigma^-$	$^5\Pi$	$^6\Sigma^+$	$^5\Delta$	$^4\Sigma^-$	$^3\Sigma^-$	$^2\Pi$	$^3\Pi$
d	B3LYP	1.830	1.761	1.709	1.723	1.752	1.735	1.739	1.870	2.041	1.937
	BLYP	1.848	1.779	1.727	1.740	1.771	1.754	1.756	1.852	2.027	1.945
	B3PW91	1.821	1.752	1.702	1.716	1.741	1.722	1.726	1.858	2.029	1.920
	BPW91	1.835	1.767	1.716	1.729	1.756	1.738	1.739	1.838	2.013	1.925
	B3P86	1.819	1.751	1.700	1.713	1.739	1.721	1.723	1.851	2.019	1.915
	BP86	1.837	1.768	1.717	1.729	1.757	1.739	1.738	1.834	2.004	1.923
	SVWN	1.816	1.735$^{\#}$	1.697	1.706	1.733	1.714	1.712	1.793	1.926	1.875^{b}
	MPW1PW91	1.817	1.749	1.698	1.713	1.737	1.718	1.722	1.867	2.031	1.919
	PBE1PBE	1.816	1.749	1.697	1.712	1.737	1.718	1.721	1.864	2.030	1.918
	Expt.	1.790^{c}	1.7116^{d}	1.691^{d}						2.003^{c}	
	Theor.	1.82^{e}	1.74^{e}	1.71^{e}	1.72^{e}	1.76^{e}	1.75^{e}	1.74^{e}	1.85^{e}	2.12^{f}	
		1.811^{g}	1.723^{g}	1.697^{g}	1.80^{f}				1.70^{f}	2.06^{i}	
					1.71^{h}				1.95^{h}		
					1.76^{i}						
ω	B3LYP	857.9	929.8	982.9	920.6	877.2	858.2	799.1	567.5	456.2	375.2
	BLYP	825.8	894.4	945.3	893.5	841.1	824.8	778.6	630.2	444.6	350.9
	B3PW91	869.6	940.8	992.3	922.3	893.5	878.6	819.3	580.4	463.1	401.4
	BPW91	843.1	910.2	960.4	905.0	864.6	850.8	802.1	649.8	450.1	380.7
	B3P86	872.7	944.5	998.2	933.0	898.5	883.3	826.2	595.9	469.8	409.2
	BP86	841.2	909.5	961.9	909.3	864.9	852.0	806.0	658.4	456.1	383.8
	SVWN	871.3	985.4$^{\#}$	1001.9	956.2	908.4	897.5	855.1	720.6	518.5	654.1^{b}
	MPW1PW91	875.3	948.3	998.9	920.4	899.6	885.1	823.1	559.9	466.9	409.2
	PBE1PBE	875.7	948.2	1000.5	923.2	900.4	886.3	823.1	563.9	467.7	408.0
	Expt.	861^{c}	969.8^{c}	989^{c}						490^{c}	
	Theor	855^{g}	970^{g}	977^{g}	560^{f}				380^{f}	461^{f}	
					1035^{h}				470^{h}		
D_e	B3LYP	6.760	7.390	7.180	4.955	5.141	4.656	3.739	2.290	1.825	0.871
	BLYP	7.240	7.943	7.857	5.738	6.418	5.238	4.600	3.094	2.151	1.033
	B3PW91	6.864	7.570	6.963	4.659	5.110	4.611	3.702	2.258	1.771	0.910
	BPW91	7.391	8.184	7.614	5.394	5.813	5.394	4.576	3.055	2.090	1.077
	B3P86	7.041	7.733	7.259	4.955	5.304	4.816	3.909	2.386	1.913	0.998
	BP86	7.464	8.234	7.890	5.704	5.976	5.392	4.745	2.939	2.217	1.136
	SVWN	8.730	9.515$^{\#}$	9.178	6.900	7.083	6.739	6.223	3.627	2.991	1.945^{b}
	MPW1PW91	6.720	7.415	6.790	4.449	4.942	4.417	3.470	2.146	1.709	0.896
	PBE1PBE	6.744	7.440	6.871	4.526	5.021	4.449	3.561	2.196	1.753	0.920
	Expt.	7.337^{c}	7.910^{c}	7.858^{c}	5.0^{c}		4.2^{c}	4.2^{c}	2.918^{c}	2.29^{c}	
	Theor	6.422^{e}	7.138^{e}	6.925^{e}	4.410^{e}	4.319^{e}	4.362^{e}	3.313^{e}	2.068^{e}		
		6.583^{g}	7.159^{g}	6.830^{g}	2.13^{f}				2.393^{j}	1.23^{f}	
					3.67^{h}						
IP	B3LYP	6.418	7.467	8.118	7.695	8.776	9.169	9.160	9.086	9.674	9.028
	BLYP	6.324	6.922	7.412	7.463	8.555	8.884	9.082	9.146	9.359	8.911
	B3PW91	6.275	7.523	8.220	7.717	8.780	8.948	9.097	8.998	9.551	8.920
	BPW91	6.249	6.957	7.542	7.600	8.690	8.995	9.120	9.140	9.330	8.889
	B3P86	6.822	8.059	8.763	8.267	9.351	9.518	9.684	9.614	10.205	9.503
	BP86	6.408	7.102	7.669	7.700	8.796	9.131	9.271	9.317	9.525	9.041
	SVWN	6.890	7.600$^{\#}$	8.151	8.151	9.319	9.719	9.888	9.929	10.284	9.886^{b}
	MPW1PW91	6.254	7.525	8.214	7.714	8.741	8.900	8.984	8.970	9.405	8.876
	PBE1PBE	6.243	7.478	8.172	7.562	8.707	8.862	8.966	8.927	9.391	8.840
	Expt.	5.85^{k}									
EA	B3LYP	1.366	1.316	1.213	1.294	0.872	1.499	1.552	1.372	1.529	2.041
	BLYP	1.253	1.220	1.127	1.256	1.381	1.496	1.609	1.779	1.779	2.162
	B3PW91	1.243	1.132	0.993	1.167	1.125	1.297	1.430	1.271	1.324	1.925
	BPW91	1.189	1.083	0.938	1.129	1.101	1.345	1.563	1.762	1.729	2.149
	B3P86	1.778	1.697	1.571	1.687	1.744	1.892	2.012	1.868	1.941	2.541
	BP86	1.384	1.315	1.188	1.289	1.390	1.582	1.765	1.945	1.939	2.358
	SVWN	1.812	1.790$^{\#}$	1.667	1.836	1.976	2.161	2.288	1.985	2.723	2.882^{b}

Table 2 continued

S	YO	ZrO[a]	NbO	MoO	TcO	RuO	RhO	PdO	AgO	CdO
	$^2\Sigma^+$	$^3\Delta$	$^4\Sigma^-$	$^5\Pi$	$^6\Sigma^+$	$^5\Delta$	$^4\Sigma^-$	$^3\Sigma^-$	$^2\Pi$	$^3\Pi$
MPW1PW91	1.230	1.109	0.969	1.153	1.075	0.954	1.083	1.158	1.159	2.432
PBE1PBE	1.258	1.131	0.988	1.125	1.094	0.925	1.056	1.147	1.159	2.407
Expt.								1.672 ± 0.005[l]		

[a] $S = 1$ ($^1\Sigma^+$)

[b] Previous theoretical values shown in this table are from singlet ($^1\Sigma^+$) state (which is ground states) for ZrO, differ from our calculation in which triplet state is ground state

[c] Ref [33]

[d] Ref [35]

[e] Ref [10], theoretical study by modified coupled pair functional (MCPF) method.

[f] Ref [12], theoretical study by configuration interaction plus Davidson's correction (CI + Q) for PdO and AgO. For MoO, complete active space self-consistent field (CASSCF) is used

[g] Ref [11], theoretical study by MCPF method

[h] Ref [12], theoretical study by singles and doubles excitation CI (SDCI) for MoO, multireference configuration interaction (MRCI) for PdO

[i] Ref [13], theoretical study by MCPF method

[j] Ref [10], theoretical study by single and double excitation coupled cluster with perturbative triples (CCSD(T)) method

[k] Ref [34]

[l] Ref [15], experimental study by photoelectron spectroscopy

Table 3 Calculated bond distances d (Å) and vibrational frequency ω (cm^{-1}) of cationic MO at ground state

	S	YO^+	ZrO^+	NbO^+	MoO^+	TcO^+	RuO^+	RhO^+	PdO^+	AgO^+	CdO^+
		$^1\Sigma^+$	$^2\Delta$	$^3\Sigma^-$	$^4\Sigma^-$	$^5\Pi$	$^4\Delta$	$^3\Sigma^-$	$^4\Sigma^-$	$^3\Sigma^-$	$^2\Pi$
d	B3LYP	1.783	1.715	1.676	1.652	1.712	1.773[a]	1.679	1.819	2.209	2.047
	BLYP	1.802	1.741	1.693	1.670	1.718	1.719	1.703	1.823	2.115	2.059
	B3PW91	1.774	1.707	1.669	1.646	1.708	1.685	1.784[b]	1.808	2.219	2.035
	BPW91	1.791	1.728	1.681	1.660	1.707	1.705	1.689	1.808	2.114	2.043
	B3P86	1.773	1.706	1.668	1.643	1.701	1.683	1.666	1.802	2.163	2.025
	BP86	1.792	1.730	1.683	1.660	1.706	1.706	1.690	1.805	2.093	2.038
	SVWN	1.773	1.712	1.665	1.639	1.680	1.684	1.667	1.766	1.977	1.984
	MPW1PW91	1.771	1.703	1.665	1.643	1.719	1.680	1.785[b]	1.814	2.313	2.035
	PBE1PBE	1.770	1.702	1.664	1.642	1.716	1.679	1.783[b]	1.811	2.287	2.033
ω	B3LYP	923.6	1018.9	1045.0	1111.7	799.0	777.8[a]	936.4	641.7	195.2	476.8
	BLYP	885.3	950.5	1001.7	1057.3	881.1	892.6	887.2	666.2	338.2	483.2
	B3PW91	936.7	1030.6	1045.6	1127.4	799.8	964.7	719.4[b]	651.0	175.4	483.2
	BPW91	903.4	969.6	1020.4	1079.8	890.7	917.3	911.6	681.9	326.7	493.3
	B3P86	940.3	1034.2	1060.5	1131.9	824.9	969.6	963.1	665.4	227.1	497.2
	BP86	901.9	968.4	1020.7	1079.6	900.6	917.3	912.8	689.1	348.3	498.4
	SVWN	932.1	1002.1	1058.0	1119.2	968.6	964.5	964.1	749.3	431.4	530.8
	MPW1PW91	944.5	1039.6	1063.3	1138.7	694.4	976.7	703.3[b]	616.5	128.5	473.9
	PBE1PBE	944.1	1041.4	1064.2	1139.4	706.5	978.3	708.6[b]	625.4	140.9	479.6

[a] $S = 6$ ($^6\Sigma^+$)

[b] $S = 5$ ($^5\Delta$)

From Table 1, it is seen that for some species, extremely low-lying excited states were found. For instance, for cationic RhO^+, triplet state and quintet state is nearly isoenergetic, with triplet state slightly favored (0.01 eV lower than quintet state). This means that in this case, it is difficult to tell which state is the ground state. We cannot say that triplet state is the ground state for RhO^+ because other methods may reverse the energy order. In fact, examples can be seen from Tables 2–4. Take RhO^+ as example again. It is seen that in Table 3, B3PW91, MPW1PW91 and PBE1PBE predicted that the quintet state as the ground state, while the remaining DFT methods predicted triplet state as the ground state. For MoO^-, we found (Table 4) that quartet state is the lowest state at B3LYP, BLYP, BP86 and SVWN level, while for the remaining methods (B3PW91, BPW91, B3P86, MPW1PW91 and PBE1PBE), sextet state is the lowest. Therefore, both

Table 4 Calculated bond distances d (Å) and vibrational frequency ω (cm^{-1}) of anion MO at ground state

	S	YO^-	ZrO^-	NbO^-	MoO^-	TcO^-	RuO^-	RhO^-	PdO^{-a}	AgO^-	CdO^-
		$^1\Sigma^+$	$^2\Delta$	$^3\Sigma^-$	$^4\Pi$	$^5\Sigma^+$	$^4\Delta$	$^3\Sigma^-$	$^2\Pi$	$^1\Sigma^+$	$^2\Sigma^+$
d	B3LYP	1.870	1.792	1.735	1.740	1.755	1.750	1.747	1.852	2.154[e]	2.071
	BLYP	1.885	1.807	1.750	1.753	1.787	1.768	1.767	1.865	1.961	2.059
	B3PW91	1.860	1.783	1.729	1.771[b]	1.762	1.740	1.736	1.838	1.935	2.042
	BPW91	1.872	1.795	1.741	1.780[b]	1.774	1.754	1.752	1.850	1.939	2.028
	B3P86	1.859	1.782	1.727	1.770[b]	1.760	1.737	1.733	1.835	1.929	2.034
	BP86	1.873	1.796	1.740	1.741	1.773	1.754	1.751	1.846	1.935	2.026
	SVWN	1.852	1.776	1.719	1.718	1.748	1.728	1.723	1.811	1.882	1.963
	MPW1PW91	1.856	1.780	1.726	1.769[b]	1.760	1.809[c]	1.794[d]	1.835	1.934	2.048
	PBE1PBE	1.856	1.779	1.725	1.768[b]	1.759	1.808[c]	1.793[d]	1.834	1.933	2.049
ω	B3LYP	797.1	875.9	934.1	885.8	832.5	834.8	782.7	643.8	345.7[e]	399.0
	BLYP	773.6	848.7	904.8	861.0	811.9	807.2	766.4	607.9	489.5	438.7
	B3PW91	808.8	885.9	939.1	816.4[b]	850.5	851.0	798.3	664.2	519.8	421.5
	BPW91	787.5	862.6	915.1	805.9[b]	829.8	826.3	787.8	627.6	511.6	464.2
	B3P86	812.1	889.5	945.1	821.1[b]	857.0	857.1	812.7	671.1	528.6	430.9
	BP86	787.9	863.5	918.7	877.2	832.6	829.4	792.9	639.0	517.8	467.1
	SVWN	816.8	897.0	961.2	922.9	874.6	857.6	841.0	720.4	601.9	527.3
	MPW1PW91	814.3	891.8	943.5	818.4[b]	853.9	762.3[c]	767.8[d]	665.3	522.4	407.8
	PBE1PBE	814.3	891.8	945.4	818.6[b]	853.9	762.3[c]	767.3[d]	667.6	523.6	411.1

[a] The experimentally observed ground state is $^2\Pi_{3/2}$, see ref. 15
[b] $S = 6$ ($^6\Sigma^+$)
[c] $S = 6$ ($^6\Delta$)
[d] $S = 5$ ($^5\Sigma^-$)
[e] $S = 3$ ($^3\Pi$)

further experimental study and advanced theoretical study are necessary to classify the situation. When looking at Table 1, we found that low-lying state is not unusual for the studied species. Within the energy cutoff of 0.2 eV, of the low-lying states were found for neutral ZrO, cationic NbO^+, TcO^+, anionic MoO^-, PdO^- and AgO^-.

3.1 Neutral species

The calculated spin multiplicity at our DFT calculation is the same as those of MCPF calculation [10], except for neutral ZrO. MCPF study gives singlet ($^1\Sigma^+$) state as the ground state for neutral ZrO, differing from our calculation in which $^3\Delta$ is ground state.

YO $^2\Sigma^+$ is the ground state for the neutral species, in agreement with experiment [32], but different from previous theoretical study at MCPF level ($^2\Delta$) [10]. The calculated bond distances (Table 2) are from 1.816 Å at SVWN and PBE1PBE levels to 1.848 Å at BLYP level, close to the previous theoretical values 1.82 Å [10] and 1.811 Å [11] at MCPF level, but larger than experimental value 1.790 Å [33]. The calculated vibrational frequencies are from 825.8 cm^{-1} at BLYP to 875.7 cm^{-1} at PBE1PBE, comparable to experimental values 861 cm^{-1} [33] and previous theoretical values 855 cm^{-1} at MCPF level [11]. For the calculated dissociation energy (Table 2), BPW91 gives a value 7.391 eV, in excellent agreement with experimental value 7.337 eV [33]. The IP and EA values from different methods show similar values, respectively. For IP, all the calculated values overestimate the experimental value 5.85 eV in some amount [34].

ZrO $^3\Delta$ is the ground state for the neutral species, except at SVWN level ($^1\Sigma^+$). This differs from previous theoretical study at MCPF level, in which singlet ($^1\Sigma^+$) is the ground state [10] (only SVWN behaves the same way as MCPF in predicting the ground state). The calculated bond distances change in a narrow range from 1.735 Å at SVWN ($^1\Sigma^+$) to 1.779 Å at BLYP, slightly large than the experimental value 1.7116 Å [35]. The calculated vibrational frequency is slightly smaller than the experimental value 969.8 cm^{-1} [33] except for the one 985.4 cm^{-1} ($^1\Sigma^+$) at SVWN. In reproducing the experimental dissociation energy 7.910 eV [33], BLYP (7.943 eV) has the best performance, followed by B3P86 (7.733 eV) and BPW91 (8.184 eV). The calculated EA has a narrow range from 1.083 eV at BPW91 to 1.790 eV at SVWN. IP varies from 6.922 eV at BLYP to 8.059 eV at B3P86.

NbO $^4\Sigma^-$ is the ground state for all the nine methods. The calculated bond distances from all the methods are around 1.700 Å, close to the experimental value 1.691 Å [35]. Our calculated vibrational frequencies are close to the experimental value 989 cm^{-1} [33]. For the dissociation energy, BLYP (7.857 eV) has the best performance in reproducing the experimental value 7.858 eV.

MoO $^5\Pi$ is the ground state for the neutral MoO, in agreement with MCPF assignment ($^5\Pi$) [10]. The calculated bond distances from 1.706 Å at SVWN to 1.740 Å at BLYP are close to previous theoretical values 1.71 Å at CASSCF level [12] and 1.72 Å at MCPF level [10]. The calculated vibrational frequencies change in a narrow region from 893.5 cm^{-1} at BLYP to 956.2 cm^{-1} at SVWN, much larger than complete active space self-consistent field (CASSCF) result 560 cm^{-1} [12], but smaller than singles and doubles excitation configuration interaction (SDCI) result 1,035 cm^{-1} [12]. For the dissociation energy, DFT calculations show a scattering from 4.449 eV at MPW1PW91 to 6.900 eV at SVWN, and most of the values are comparable to the experimental data 5.0 eV [33] except for SVWN (6.900 eV). Previous theoretical results for the dissociation energy also scatter from 2.13 eV at CASSCF level [12], 3.67 eV at SDCI level [12] to 4.410 eV at MCPF level [10]. This means that more work is necessary to solve the discrepancy. For the calculated IP, the values are around 7.700 eV from different methods.

TcO $^6\Sigma^+$ is the lowest state for the neutral species. The calculated bond distance is close to previous MCPF result 1.76 Å [10]. The calculated vibrational frequencies change from 841.1 cm^{-1} at BLYP to 908.4 cm^{-1} at SVWN, in a narrow range. For the dissociation energy, DFT methods in this paper give larger values compared with the value 4.319 eV at MCPF level [10]. In particular, SVWN gives a value 7.083 eV, 2.764 eV larger than 4.319 eV [10]. Nevertheless, except for the values at B3P86 and SVWN, the values for IP and EA at other methods are similar, respectively.

RuO $^5\Delta$ is the ground state for neutral species. The predicted bond distances from the current DFT methods are close to MCPF result 1.75 Å [10]. For the dissociation energy, MPW1PW91 (4.417 eV) and PBE1PBE (4.499 eV) give better result compared with the experimental data 4.2 eV [33].

RhO $^4\Sigma^-$ is the ground state. For each method, the calculated bond distance is almost the same as in RuO. For the dissociation energy, SVWN (6.233 eV) gives larger value compared with the other methods. BPW91 (4.576 eV) gives the best dissociation energy compared with the experimental data 4.2 eV [33].

PdO The ground state is $^3\Sigma^-$, in agreement with experimental observation [15]. The predicted bond distances change from 1.793 Å at SVWN to 1.870 Å at B3LYP, close to the result 1.85 Å at MCPF level [10]. The calculated vibrational frequency from 559.9 cm^{-1} at MPW1PW91 to 720.6 cm^{-1} at SVWN is larger than the result 380 cm^{-1} at CI + Q level [12] and 470 cm^{-1} at MRCI level [12]. BP86 (2.939 eV) gives the best dissociation energy in reproducing the experimental data 2.918 eV [33], followed by BPW91 (3.055 eV) and BLYP (3.094 eV). This indicates that pure density functional methods are superior to hybrid density functional methods (B3LYP, B3PW91 and B3P86) in predicting the dissociation energy in PdO. For EA, BPW91 and BLYP give values 1.762 and 1.779 eV respectively, in better agreement with the experimental value 1.672 eV [15], while the remaining methods have larger deviation compared with experimental value.

AgO $^2\Pi$ is the ground state. BP86 (2.004 Å) has the best performance in reproducing the experimental bond distance 2.003 Å [33]. For the calculated vibrational frequency, SVWN (518.5 cm^{-1}) has the best performance compared with the experimental data 490 cm^{-1} [33]. All DFT methods have reasonable performance in reproducing the experimental vibrational frequency 490 cm^{-1} [33] and previous theoretical value 461 cm^{-1} [12]. BP86 (2.217 eV) have the best performance in predicting the experimental dissociation energy 2.29 eV [33].

CdO There are no data either experimentally or theoretically available for CdO (including both neutral and charged species). $^3\Pi$ is the lowest state for DFT methods except SVWN. At SVWN, singlet state is predicted to be the ground state. The calculated bond distances change in a narrow range from 1.915 Å at B3P86 to 1.945 Å at BLYP, except for 1.875 Å at SVWN ($^1\Sigma^+$). The calculated frequency is the smallest compared with its neutral partners.

From Table 2, we can see that the calculated vibrational frequency increases from YO, ZrO to NbO, then decreases with the increases of the atomic number. This is different from 3d transition metal monoxides in which only increase trend is observed from CuO to ZnO [7].

3.2 Charged species

For YO$^-$, the calculated ground state is $^1\Sigma^+$, different from experimental observation $^3\Delta$. The experimentally

Table 5 Ground state occupations of the neutral and charged 4d-metal monoxides

Neutral			Cation			Anion		
	State	Electronic configuration		State	Electronic configuration		State	Electronic configuration
YO	$^2\Sigma^+$	$11\sigma^2 12\sigma^1 5\pi^4$	YO^+	$^1\Sigma^+$	$11\sigma^2 5\pi^4$	YO^-	$^1\Sigma^+$	$11\sigma^2 12\sigma^2 5\pi^4$
ZrO	$^3\Delta$	$11\sigma^2 12\sigma^1 5\pi^4 2\delta^1$	ZrO^+	$^2\Delta$	$11\sigma^2 5\pi^4 2\delta^1$	ZrO^-	$^2\Delta$	$11\sigma^2 12\sigma 25\pi^4 2\delta^1$
NbO	$^4\Sigma^-$	$11\sigma^2 12\sigma^1 5\pi^4 2\delta^2$	NbO^+	$^3\Sigma^-$	$11\sigma^2 5\pi^4 2\delta^2$	NbO^-	$^3\Sigma^-$	$11\sigma^2 12\sigma^2 5\pi^4 2\delta^2$
MoO	$^5\Pi$	$12\sigma^1 5\pi^4 6\pi^1 2\delta^2$	MoO^+	$^4\Sigma^-$	$11\sigma^2 12\sigma^1 5\pi^4 2\delta^3$	MoO^-	$^4\Pi$	$12\sigma^2 5\pi^4 6\pi^1 2\delta^2$
TcO	$^6\Sigma^+$	$12\sigma^1 5\pi^4 6\pi^2 2\delta^2$	TcO^+	$^5\Pi$	$12\sigma^1 5\pi^4 6\pi^1 2\delta^2$	TcO^-	$^5\Sigma^+$	$12\sigma^2 5\pi^4 6\pi^2 2\delta^2$
RuO	$^5\Delta$	$12\sigma^1 5\pi^4 6\pi^2 2\delta^3$	RuO^+	$^4\Delta$	$11\sigma^2 5\pi^4 6\pi^2 2\delta^3$	RuO^-	$^4\Delta$	$12\sigma^2 5\Pi^4 6\pi^2 2\delta^3$
RhO	$^4\Sigma^-$	$12\sigma^1 5\pi^4 6\pi^2 2\delta^4$	RhO^-	$^3\Sigma^-$	$11\sigma^2 5\pi^4 6\pi^2 2\delta^4$	RhO^-	$^3\Sigma^-$	$12\sigma^2 5\pi^4 6\pi^2 2\delta^4$
PdO	$^3\Sigma^-$	$12\sigma^2 5\pi^4 6\pi^2 2\delta^4$	PdO^+	$^4\Sigma^-$	$12\sigma^1 5\pi^4 6\pi^2 2\delta^4$	PdO^-	$^2\Pi$	$12\sigma^2 5\pi^4 6\pi^3 2\delta^4$
AgO	$^2\Pi$	$12\sigma^2 5\pi^4 6\pi^3 2\delta^4$	AgO^+	$^3\Sigma^-$	$12\sigma^2 5\pi^4 6\pi^2 2\delta^4$	AgO^-	$^1\Sigma^+$	$12\sigma^2 5\pi^4 6\pi^4 2\delta^4$
CdO	$^1\Sigma^+$	$12\sigma^2 5\pi^4 6\pi^4 2\delta^4$	CdO^+	$^2\Pi$	$12\sigma^2 5\pi^4 6\pi^3 2\delta^4$	CdO^-	$^2\Sigma^+$	$13\sigma^1 5\pi^4 6\pi^4 2\delta^4$

observed ground electronic state for PdO^- is $^2\Pi_{3/2}$, in agreement with our calculation $^2\Pi$. Compared with 3d transition metal monoxides [7], only RuO^+ ($^4\Delta$) and RhO^+ ($^3\Sigma^-$) at B3LYP in our calculation (Tables 3 and 4) have different electron configuration compared with their corresponding congeners FeO^+ ($^6\Sigma^+$) and CoO^+($^5\Delta$).

From Tables 2–4, comparing with hybrid density functional methods B3LYP, B3PW91 and B3P86, we can notice that pure density functional methods BLYP, BPW91 and BP86 show longer bond distances (except for PdO, AgO, AgO^+ and CdO^-), lower vibrational frequency (except for PdO, TcO^+, PdO^+, AgO^+, CdO^+ and CdO^-) and larger dissociation energy from YO to CdO as well as their cations and anions. For most of the species, hybrid density functional methods give larger IP and EA compared with pure density functional methods (Table 2).

From Tables 2–4 we also noticed that for most species (including neutral and charged species) BLYP gives the longest bond distance compared with other density functional methods, while SVWN gives the shortest bond distance. Meanwhile, SVWN also presents the largest dissociation energy and EA compared with other DFT methods (Table 2). In addition, MPW1PW91 and PBE1PBE show the same performance in predicting the bond distances and vibrational frequencies, i.e., they tend to produce the same bond distance and vibrational frequencies for the studied species. The bond distances from B3PW91 are nearly the same as those from B3P86 (Tables 2–4). It is also true between BPW91 and BP86 in predicting the bond distance.

3.3 Bonding analysis

The calculated ground state electron configuration for most of the density functional methods is listed in Table 5. The calculated dipole moment of the neutral species at B3LYP from YO to CdO is 5.22, 4.57, 4.05, 3.75, 4.27, 4.16, 4.13, 4.27, 5.01, and 2.99 D. These calculated dipole moments suggest that the bonding patterns are complex for these systems which involve covalent, ionic and dative components. For instance, if the bonding is purely ionic, the dipole moment of YO will be 8.93 D, but it is only 5.22 D. This indicates that other components of the bonding exist besides ionic component. Normally, the bonding for the title molecules mainly arises from interactions between metal d and s orbitals and oxygen 2p orbital. The metal σ orbital undergoes sd_σ hybridization and interacts with oxygen $2p_\sigma$ orbital to form bonding, nonbonding and antibonding orbitals. The metal $4d_\pi$ orbitals interact with oxygen $2p_\pi$ orbitals to give bonding and antibonding orbitals. The metal $4d_\delta$ orbitals are nonbonding because there are no corresponding orbitals in oxygen. Although the expected order of stability is σ bond > π bond > σ and δ nonbonding > π antibonding > σ antibonding, the filling order is complicated due to the fact that d–d exchange energy is larger than the energy separation between different orbitals and the mixings of the metal s^2d^n and s^1d^{n+1} asymptotes.

From Table 5, it can also be seen that the spin multiplicity is very regular for neutral and anionic species. We also noted that the spin multiplicity of charged species is obtained by −1 compared with the corresponding neutral species from YO to RhO. For PdO and AgO, the spin multiplicity of cations is obtained by +1 compared with their neutral partners, while anions by −1. For CdO, the spin multiplicity of charged species is obtained by +1 compared with neutral species. Compared with 3d metal monoxides [7], we see that the spin multiplicity is the same for most of the species except for RuO^+ and RhO^+. The bonding patterns are also quite similar for most of the species.

4 Conclusions

Density functional methods B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, SVWN, MPW1PW91 and PBE1PBE have been tested in the study of the spectroscopic constants for 4d transition metal monoxides. The calculated properties are found to be dependent on the functionals employed. MPW1PW91 and PBE1PBE tend to produce the same bond distance and vibrational frequency for the studied molecules. The dissociation energies they produced are also extremely close, and this kind of situation occurs similarly on ionization potential and electron affinity. B3PW91 and B3P86 predicted nearly the same bond distance. This is also true for BPW91 and BP86. For neutral species except TcO and RuO, pure density functional methods BLYP, BPW91 and BP86 have good performance in predicting dissociation energies than hybrid density functional methods B3LYP, B3PW91 and B3P86. Furthermore, BLYP gives the longest bond distance, while SVWN gives shortest bond distance, largest dissociation energy and EA. For some species, low-lying states were found to be the competitive candidate for the ground state. In this case, further experimental study and theoretical study are necessary to get new insights. For the ground state, the spin multiplicity of the charged species can be obtained by ±1 of their corresponding neutral species. Finally, we hope this study will serve as a useful guide for experimental studies, especially for those molecules with no other data is available and provide guidance in choosing density functional methods in further theoretical study.

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